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WADD TECHNICAL REPORT 60-782 PART II

VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURE

Part II. Mass Spectrometric Studies of the Vaporization of Sulphides and the Dissociation Energy of S₂

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WRIGHT AIR DEVELOPMENT DIVISION

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Materials Central Contract No. AF 61(052)-225 Project No. 7350

WRIGHT AIR DEVELOPMENT DIVISION
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

FOREWORD

This report was prepared by the University of Brussels, Belgium, under USAF Contract No. AF 61(052)-225. The contract was initiated under Project No. 7350, "Refractory Inorganic Nonmetallic Materials," Task No. 73500, "Ceramic and Cermet Materials Development". The work was administered under the directorate of Advanced Systems Technology, Wright Air Development Division, with Mr. F. W. Vahldiek acting as project engineer.

This report covers work conducted from March 1959 through March 1960.

The authors wish to thank the Comite Belge de Spectrometrie de Masse (I.R.S.I.A.) which made available part of the equipment used in this report.

ABSTRACT

The equilibria $S_2 \Rightarrow 2s$ and $CaS \Rightarrow Ca + S$ have been observed in the vapor phase above CaS. $D_0(S_2) = 4.4 \pm 0.2$ e.v., $D_0(S_2) = 5.9 \pm 0.2$ e.v., have been determined mass spectrometrically.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

W. G. RAMKE

Chief, Ceramics and Graphite Branch Metals and Ceramics Laboratory

Materials Central

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WADD TR 60-762 Pt 11

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MASS SPECTROMETRIC STUDIES OF THE VAPORIZATION OF SULPHIDES AND THE DISSOCIATION ENERGY OF S2.

DISCUSSION

The disagreement between second and third law values of the dissociation energy of $S_2(D_c^o(S_2))$ obtained from equilibrium measurements has been emphasized many years ago (1). A relationship was also pointed out between the heat of combustion of SO, $D_o^o(O_2)$, $D_o^o(SO)$, and $D_o^o(S_2)$, which should permit one to choose one of the values allowed by observed predissociations for $D_o^o(S_2)$ and $D_o^o(SO)$. Recent measurements do not seem to settle the question (3).

In the vapour phase above CaS we have coserved by mass spectrometry the dissociation $S_2 \rightleftharpoons 2S$, and $CaS \rightleftharpoons Ca + S$ and have calculated $D_{\bullet}^{\circ}(S_2) = 4.4 \pm 0.2$ e.v., $D_{\circ}^{\circ}(SO) = 5.4 \pm 0.2$ e.v. $D_{\circ}^{\circ}(CaS) = 3.7 \pm 0.2$ e.v. and $\Delta H_{298}^{\circ}(CaS) = 5.9 \pm 0.2$ e.v.

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WADD TR 60-782 Pt II 1

The mass spectrometric method has been described previously (4,5). The sample was heated in a molybdenum Knudsen cell : provisions were made to distinguish between residual gas molecules and those of the beam which passes through a cooled collimation system : ion intensities were measured with an electron multiplier. Absolute values of partial vapour pressures were obtained from P = I T/S; ; I is the measured current corresponding to a species 1, I the absolute temperature of the Knudsen cell, and S, the sensitivity for i: $S_1 = (M_1/2MR)^{1/2} (s/c_1) \sum I_1 I^{1/2} \Delta t; M_1 is its$ molecular mass, R the gas constant, s the area of the effusion crifice and t the time necessary to evaporate the weight G, of species i . Brightness temperatures of a small threaded hole at the bottom of the Knudsen cell have been measured with an optical pyrometer; emissivity and window corrections were made. (7)

Dissociation energies were calculated from: $D_0^{\circ} = - RT \ln K + T \Delta ((F_T^{\circ} - H_0^{\circ})/T)$ (3d law) and: $D_T^{\circ} = Rd \ln K/d(1/T)$ (2d law) using free energy functions taken from Stull and Sinke (8), or for Cas, calculated by comparison of oxides and sulphides, assuming $\omega = 390$ cm⁻¹, r = 2.3 A and that only the Σ ground state is important.

Otvos and Stevenson and it was assumed that those of molecules are equal to the sum of those of the constituent atoms. The mass effect and the molecular effect of the multiplier were considered to compensate each other. A possible error of 20° in the temperature measurement would lead to an uncertainty of 12% in the second law and of 1% in the third law values; instead of the assumptions made above, it may be reasonable that the product of ionization cross section and multiplier gain is the same for the atom and for the molecule (11):

in that case the 3d law D_0^0 values of Table I are increased by about + 3.5 kgal. and $\Delta H_{298}^{vap}(Cas)$ diminished by the same amount.

The data of Table I and $\triangle H_{298}^{\text{vap}}(\text{Ca})^{(8)} = 42.2 \text{ kcal}$. $\triangle H_{298}^{0}(1/2 \text{ S}_{2}) = 15.4 \text{ kcal}$, the standard heat of formation $\triangle H_{298}^{0}$ f. $(\text{CaS}) = 110.0 \pm 2 \text{ kcal}^{(12)}$ permit one to calculate $\triangle H_{298}^{\text{vap}}(\text{CaS}) = 136 \text{ kcal}$. The value obtained from this cycle is considered as more reliable than that given in table I (see remark table I).

 $D_0^{C}(S_2)$ obtained here, combined with $\Delta H_0^{C}(SO)^{(2b)}$ for the reaction 1/2 $S_2 + 1/2$ 0 = SO definitely rules out a value $D_0^{C}(SO)$ smaller than 5.2 e.v.

There are good spectroscopic arguments for $D_0^{C}(SO) = 5.358$ e.v. rather than 5.027 e.v. (3).

Our measurements are not accurate enough to permit one to settle the question whether the prediscretation at 4.41 e.v. gives the exact dissociation of $S_2^{(14)}$ or an upper limit (15); a value $D(S_2) = 4.2$ e.v. would agree with our results (16). Within the accuracy quoted in Table I, all available data

on $D(S_2)$ and $D(SO)^{(3)}$ except appearance potential measurements (17) and older equilibrium measurements (cf. 1,2,3,14) seem to be in agreement.

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Table I. Heats of Vaporization and Dissociation Energies of S2 and CaS

T ^C K	logp(S)*	logp(S ₂	logp(Ca)	logp(Ca	$D_0^0(S_2)$ kcal	D ^C (Cas) o. kcal	Hvap(CaS) kcal
	-						
1922	- 5.96	- 6.56	- 6.15	٠_	100	-	-
1975	-5.46	- 6.25	-5.79	-	96.5	-	-
2026	- 5•34	-6.01	-5.54	-	98.0	= =	-
2048	-5.04	- 5.82	- 5.35	-	96.4	-	-
2053	-5. 03	-5.83	-5.32	-7.26	96.4	79.8	151.9
2070	-5.18	- 5.88	-5.42	-7.03	98.8	84.9 *	149.0
2098	-4.86	- 5.63	-5.13	-6.99	97•3	80.7	151.5
2143	-4.76	-5.4 8	-5.03	-6.66	98.9	83.7	151.6
2144	-4.60	- 5.38	-4.90	-6.72	96.7	80.3	152.2
2154	-4.71	-5.44	-4.99	-	98.8	-	-
2156	-4.64	- 5.38	-4.86	-6.71	96.8	80.1	152.9
a190	- 4.52	- 5.28	- 4.75	-6.55	98.3	81.5	153.6
2223	-4.27	-5.02	-4.58	- 6.27	97.4	81.3	153.7
2297	-3.9 8	-4.82	-4.24	-5.99	96.8	80.3	155.6
			averag	e e	97.6	81.4	152.4**
			slope	method	108	95	129
	(propos	sed values		101 🛨 5	86 ± 5	136 🛨 10

m Decimal logarithms of pressures in atmospheres.

Fr - H 298 /T for this process in based on very scanty data on Cp (CaS) (K. K. Kelley, U.S. Bareau of Mines Bulletin 476, Washington D. C., 1949)

			VAPURIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURE, Part II Mess Spectrometric Studies of the Vaporization of Sulphides and the Dissociation Energy of Sp. by R. Colin, P. Goldfinger and M. Jeunehomms. November 1960 Spp. table. (Froject No. 7550; Task 7550) (WADD TR 60-782 Ft II)(Contract No. 37 61(92)-225. Unclassified report The equilibria Spc 25 and CaS = Ca+5 have been observed in the vapor phase above CaS. D((Sp)=4,440.2 e.v., D((SO)=5,440.2 e.v., D((SS)=7,720.2 e.v., and Albjog(CaS)=5.92.0.2 e.v. have been determined.	DISTURBATIVE OF EDUSCRIA, Educada, Helpfum
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UNIVERSITY OF ERUSSELS, Erussels, Belgium VAPURIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURE, Part II Mass Spectrometric Studies of the Vaporization of Sulphides and the Dissociation Energy of S₂, by R. Colin, F. Goldfinger and M. Jeunehomme. November 1960 Spp. table. (Project No. 7350; Task 73500)(wADD TR 60-782 Ft II)(Contract No. AF 61(052)-225. 0.2 e.v. have been determined. The equilibria S. 25 and CaS = Ca+S have been observed in the vapor phase above CaS. [Sc]=4.4±0.2 e.v., Do(SO)=5.4±0.2 e.v., Do(CaS)=3.7±0.2 e.v., and \(\D \) H298 (CaS)=5.9± Unclassified report (over + UNCLASSIFIED UNCLASSIFIED The equilibrie S. 2S and CaS = Ca+S bave been observed in the vapor phase above CaS. Da(S2)=4.410.2 e.v.. Da(S0)=5.440.2 e.v.. Da(CaS)=3.710.2 e.v. and AH268(CaS)=5.91 Sulphides and the Dissociation Energy of S., by R. Colin, P. Goldfinger and M. Jeunshomme. November 1960 Spp. table. (Froject No. 7550; Task 75500)(*ADD TH 60-702 Ft II)(Contract No. AF 61(052)-225. 0.2 e.v. have been determined. HIGH TEAPERATURE, Part II Mess Spectro-metric Studies of the Vaporization of UNIVERSITY OF ERUSSELS, Erussels, Belgium VAPORIZATION OF CONFOUNDS AND ALLOYS AT (over) UNCLASSIFIED UNCLASSIFIND

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UMIVERSITY OF ERUSSELS, brussels, beights VAPOHIZATION OF COMPOUNDS AID ALLOYS AT HIGH TEMPERATURE. Part II Mess Spectrometric Studies of the Vaporization of Sulphdes and the Dissociation Energy of S ₂ , by R. Colin, P. Goldfinger and M. Jeunehorme. November 1960 8pp, table. (Froject No. 7350; Task 73500)(*ADD TH 60-752 Ft II)(Contract No. AF 61(052)-225. Unclassified report The equilibris S ₂ . 725 and CaS = Ca+S have been observed in the vapor phase above CaS. D**(CaS)=3.740.2 e.v., D**(CSO)=5.440.2 e.v., D**(CSO)=5.94.0.2 e.v., have been determined.	
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0.2 e.v. have been determined.	UNIVERSITY OF HRUSSELS, Equated in Belgium VAPOHIZATION OF COMPOUNDS AND ALLOYS AT HIGH TRAPPHARUES, Part II Mass Spectrometric Studies of the Vaporization Energy of Sulphides and the Dissociation Energy of S2, by R. Colin, P. Goldfinger and M. Jeunehomme. November 1960 8pp. table. (Froject No. 7)50; Task 7)500)(WADD TR 60-732 Ft II)(Contract No. AF 61(052)-225. Unclassified report The equilibris S2-25 and CaS = Ca+S have been observed in the vapor phase above CaS. D2(65)=4,410.2 e.v. and A HJSE(CaS)=5,95	
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